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EFFECT OF MINERALIZERS ON THE SYNTHESIS OF CERAMIC PIGMENTS FROM TALC

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The mineralizing effect of sodium fluoride, boric acid, and a natural fluorine-bearing mineral (topaz concentrate) on the synthesis from talc of ceramic pigments with magnesium metasilicate, forsterite, and diopside structures is investigated. It is shown that NaF is the most active mineralizer. It is noted that NaF has a positive effect not only on the synthesis of crystalline structure but also on the chromaticity of the pigments. The pigment compositions developed can be widely used to tint ceramic pastes, glazes and glasses, in the manufacture of building materials, and to make paints.

Key words: ceramic pigments, synthesis, talc, mineralizers.

Substances that accelerate phase-formation reactions — mineralizers — are often used to obtain ceramic pigments under industrial and laboratory conditions. The effectiveness of mineralizers depends on their nature, quantity, and degree of dispersion in the reagent being activated [1].

The following possibilities for the action of mineralizers are known: protection from resorption of a mineral, creation of artificial rudimentary crystalline grains, action similar to that of a catalyst, formation of solid solutions, and action similar to fluxes.

To intensify many reactions in the solid phase, the content of an added mineralizer must be not exceed 1 – 3% of the total mass of the mixture. Boron, fluorine, and alkali-metal compounds are used as mineralizers to make ceramic pigments.

The mineralizing action of fluorine ions is explained by the fact that they cannot participate in the formation of "bridges" between the silicon-oxygen tetrahedra. When fluorine ions are introduced into the initial mix, the fraction of oxygen atoms which are bound in the space lattice between one another via silicon atoms, changes, i.e., a fluorine ion breaks chemical bonds in a crystal lattice.

Boron compounds are often used as mineralizing additions in the synthesis of pigments. It has been observed that B_2O_3 lowers the sintering temperature of many crystalline materials, since B^{3+} has a large charge and a small ionic radius (0.02 nm). Consequently, the polarization power is more strongly expressed for boron than for singly charged alkali-metal ions; B^{3+} has a greater effect on decreasing the stability of the crystal lattice. It is also observed that B_2O_3 has a positive effect on the chromophoric properties of pigments [1].

Currently, a promising direction of research is to study the possibility of obtaining ceramic pigments using natural mineral raw materials. The structures of many pigments which are conventionally synthesized from pure oxides and salts of various elements can be obtained from chemically pure natural raw materials, for example, diopside, wollastonite, and others [2]. But, a structural deficiency of natural minerals is their organic capability of incorporating tinting ions. The introduction of mineralizers can loosen their crystal lattice, increase the "ionic capacity" of natural minerals, and improve the color characteristics of ceramic pigments based on natural mineral raw materials [3].

We investigated the effect of different mineralizers on the synthesis of ceramic pigments with magnesium metasilicate, forsterite, and diopside structures by means of talc.

Talc is a natural mineral that is widely used in technology. When talc is heated, magnesium metasilicate and free silica are formed. To bind silica and increase the yield of magnesium metasilicate, talc is blended with magnesium oxide according to the reaction

$$3MgO \cdot 4SiO_2 \cdot H_2O + MgO = 4(MgO \cdot SiO_2) + H_2O. \quad (1)$$

The forsterite structure can also be obtained by blending talc with magnesium oxide:

$$3MgO \cdot 4SiO_2 \cdot H_2O + 5MgO = 4(2MgO \cdot SiO_2) + H_2O. \quad (2)$$

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TABLE 1.

Raw material	Mineral content, wt.%	Content, wt.%						
		SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	R_2O	calcination losses
Slyudanskoe wollastonite	95	51.70	0.11	46.48	1.23	–	0.16	0.32
Onotskoe talc	98	61.27	0.61	0.50	32.23	0.41	–	4.98

TABLE 2.

Pigment*	Chromophore content, mole	Mineralizer	Color	Chromaticity coordinates			Wavelength, nm	Tone purity, %
				x	*y*	*z*		
Pigments with magnesium metasilicate structure								
M-10	1.0 NiO	NaF	Yellow-green	0.38	0.38	0.24	578	36
M-14	0.7 Cr_2O_3	B_2O_3	Grass-green	0.34	0.49	0.17	556	64
Pigments with forsterite structure								
F-10	1.0 NiO	NaF	Light green	0.36	0.37	0.27	574	23
F-18	0.5 Fe_2O_3	NaF	Orange	0.54	0.38	0.08	596	79
Pigments with diopside structure								
D-5	1.0 CoO	Topaz	Bright rose	0.43	0.26	0.32	502	31
D-18	0.5 Fe_2O_3	NaF	Red-brown	0.57	0.35	0.07	605	76

Wollastonite and magnesium oxide are added to talc to obtain the diopside structure:

$$3MgO \cdot 4SiO_2 \cdot H_2O + 4(CaO \cdot SiO_2) + MgO = 4(CaO \cdot MgO \cdot 2SiO_2) + H_2O. \quad (3)$$

To obtain colored crystalline compounds these reactions are conducted with the participation of chromophore oxides:

$$3MgO \cdot 4SiO_2 \cdot H_2O + (1 - x)MgO + xMeO = 4(Mg_{1-0.25x}Me_{0.25x}SiO_3) + H_2O,$$

where $x = 0.1 - 1.0$ (moles);

$$3MgO \cdot 4SiO_2 \cdot H_2O + (5 - x)MgO + xMeO = 4(Mg_{2-0.25x}Me_{0.25x}SiO_4) + H_2O,$$

where $x = 0.1 - 1.5$ (moles);

$$3MgO \cdot 4SiO_2 \cdot H_2O + 4(CaO \cdot SiO_2) + (1 - x)MgO + xMeO = 4(CaMg_{1-0.25x}Me_{0.25x}Si_2O_6) + H_2O,$$

where $x = 0.1 - 1.0$ (moles); and, MeO — chromophore-metal oxides.

We used natural mineral raw material — talc from the Onotskoe deposit and wollastonite from the Slyudyanskoe deposit. The chemical and mineral compositions of the natural materials are presented in Table 1.

Transition-metal — iron, chromium, cobalt, nickel, and copper — salts were used as chromophores. The chromophore content in the pigments in terms of the oxide varied from 0.1 to 1.5 moles.

Different mineralizers were added to the mix with exactly the same composition — topaz concentrate from the "Kopna" deposit and boric acid and sodium nitride in the amount 3 wt.%. The pigments were fired at 1100 – 1200°C.

Color analysis of the pigments obtained shows that the color of pigments with forsterite and diopside structures is brighter than that of pigments with magnesium metasilicate structure. A comparative visual analysis also showed that the color of pigments obtained by adding NaF is more saturated. The color characteristics of certain pigments (SF-256 spectrophotometer) are presented in Table 2 and their spectral reflection curves are presented in Fig. 1.

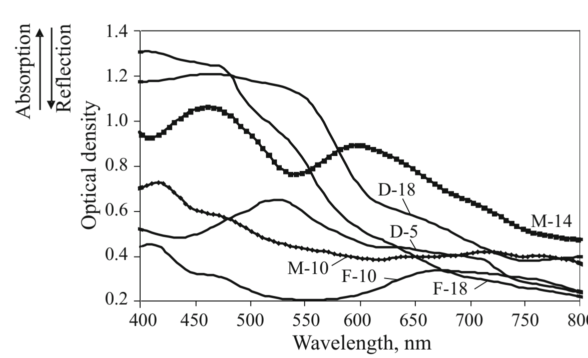

Fig. 1. Spectral reflection curves of pigments.

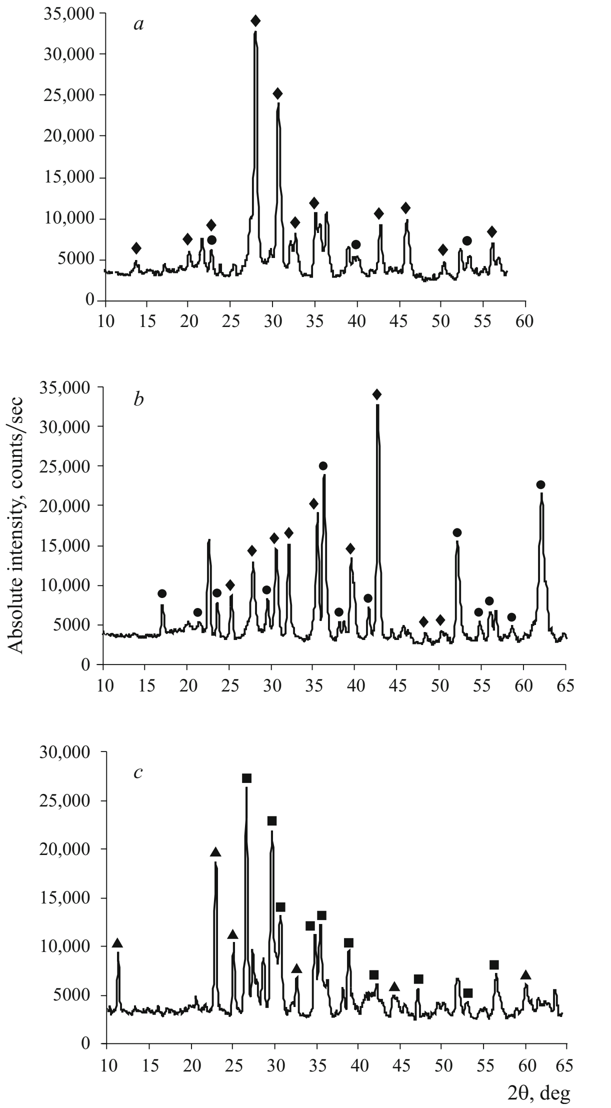

Fig. 2. X-ray diffraction patterns of free samples with no mineralizers (firing temperature 1200°C): *a*) with magnesium metasilicate structure; *b*) with forsterite structure; *c*) with diopside structure; ◆) magnesium metasilicate; ●) forsterite; ■) diopside; ▲) wollastonite.

X-ray phase analysis was performed with a DRON-3M diffractometer to determine the crystalline phase contained in the experimental samples.

It was determined that a magnesium metasilicate structure in the form of clinoenstatite ($d = 0.299$, 0.211 nm) and protoenstatite ($d = 0.316$, 0.292, 0.197 nm) forms in the samples (Fig. 2) synthesized via the reaction (1) at 1200°C. Adding sodium fluoride intensifies the formation of protoenstatite ($d = 0.292$, 0.197 nm). No substantial structural changes occur in the sample with topaz and boric acid.

Aside from forsterite ($d = 0.247$, 0.175, 0.149 nm), the sample fired at 1200°C with forsterite structure and no mineralizer contains magnesium metasilicate predominately in the form of clinoenstatite ($d = 0.299$, 0.211 nm). Adding

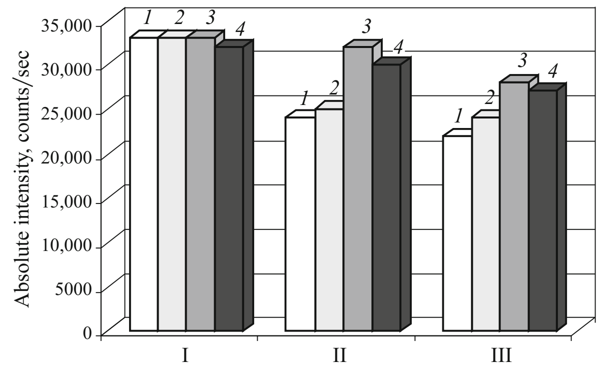

Fig. 3. Change of the absolute intensity of the diffraction peaks characteristic for magnesium metasilicate (I, $d = 0.316$ nm), forsterite (II, $d = 0.246$ nm), and diopside (III, $d = 0.299$ nm): *1*) no mineralizer; *2*) with topaz concentrate; *3*) with sodium fluoride; *4*) with boric acid.

topaz does not greatly affect the structure formation — peaks characteristic for forsterite and clinoenstatite are indexed. Adding sodium fluoride and boric acid intensifies the peaks characteristic for forsterite ($d = 0.247$, 0.175, 0.149 nm), and forsterite becomes the main phase.

Diffraction peaks for diopside ($d = 0.334$, 0.299, 0.252 nm) and wollastonite ($d = 0.782$, 0.354, 0.254 nm) are present at 1200°C in pigments with diopside structure. Mineralizers increase the intensity of the diffraction peaks characteristic for diopside. However, wollastonite peaks ($d = 0.782$, 0.354, 0.254 nm) are also present.

To analyze the mineralizing effect of topaz concentrate, sodium fluoride, and boric acid, the absolute intensities of the main diffraction peaks characteristic for magnesium metasilicate — protoenstatite ($d = 0.316$ nm), forsterite ($d = 0.246$ nm), and diopside ($d = 0.299$ nm) in the x-ray diffraction patterns of free samples obtained with and without the addition of various mineralizers were compared (Fig. 3). Analysis shows that NaF is the most active mineralizer (the intensity of the forsterite and diopside peaks increases).

The stronger mineralizing action of sodium fluoride as compared with topaz concentrate $Al_2SiO_4(F, OH)_2$ is explained by the fact that for the same amount of these substances there are three times more active fluorine ions in NaF.

It was determined that the experimental mineralizers have different effects on the synthesis of pigments. The mineralizing effect of topaz is due to the active influence of the fluoride ions in the gas phase, which are released when topaz decomposes and increase the reactivity of the mixture in the entire volume. This process is not accompanied by the formation of low-melting eutectics, as in the case of NaF and boric acid addition; pigments are obtained in the form of colored powders and not cakes, which are difficult to comminute. However, to reach the desired effect it is necessary to triple the amount of topaz concentrate introduced as compared with NaF. The latter compound was observed to have a

positive effect on the chromaticity of the pigments. This is also confirmed by published data, according to which F^- is the most effective anion influencing the brightness of pigments with Na^+ being the most effective cation [1].

The pigments obtained on the basis of the natural mineral talc possess a range of diverse colors and they are stable at high temperatures and resist fluxes. The pigment compositions which have been developed can be widely used to tint ceramic pastes, glazes, and glass, in the production of building materials, and for making paints.

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